SUPPORTING INFORMATION

Palladium(II)-Catalysed Electrophilic Cyclisation of Electron-Deficient Aromatic Enynes

Na Wu, Andréi S. Batsanov, Antonios Messinis, Andrew Whiting, Zhen Yang and Todd B. Marder

a Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education and Beijing National Laboratory for Molecular Science (BNLMS), College of Chemistry, Peking University, Beijing 10087, China
b Department of Chemistry, Durham University, South Road, Durham DH1 3LE, U.K.
† Current address: Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

todd.marder@uni-wuerzburg.de; zyang@pku.edu.cn

Contents

1. General information ................................................................. S2
2. Experimental procedures and characterisation data ........................ S3
   2.1 Synthesis of substituted styrene alkynone precursors and characterisation data ............................................... S3
   2.2 General procedure for synthesis of substituted styrene alkynone substrates and product characterisation data .......... S4
   2.3 General procedure for substituted styrene alkynone cyclisations and characterisation data ................................ S10
   2.4 Procedure for Luche reduction of cyclisation product and characterisation data ........................................ S14
   2.5 References ........................................................................ S15
3. $^1$H and $^{13}$C-NMR spectra for new compounds ......................... S16
4. X-ray molecular structures .......................................................... S89
1. General information
Reactions were performed under nitrogen unless otherwise stated. All reagents were purchased from Aldrich and used as received. Solvents (AR grade) were used as received. $^1$H NMR and $^{13}$C {$^1$H} spectra were recorded using Bruker Avance 400, Bruker DRX 500, Avance 600 or Varian VNMRS 700 spectrometers in CDCl$_3$ with residual solvent protons (7.26 ppm) or the carbon resonance (77.16 ppm) used to reference the spectra. Chromatography was carried out using silica gel (Silicagel LC60A 40-63 μm) obtained from Fluorochem. The removal of solvent was performed on a rotary evaporator under vacuum. IR spectra were recorded on a Perkin-Elmer 1615 FTRIR spectrophotometer. Melting points were determined using an Electrothermal melting point apparatus. Low resolution mass spectrometry was carried out on a Waters TQD equipped with Acquity UPLC and an electrospray ion source and high resolution mass spectrometry was performed on a Waters LCT Premier XE equipped with Acquity UPLC and a lock-mass electrospray ion source.

2. Experimental procedures and characterisation data
2.1 Synthesis of substituted styrene alkynone precursors and characterisation data
2-Vinylbenzoic acid, (E, Z)-2-styrylbenzoic acid and (E, Z)-2-(4-methylstyryl)benzoic acid were prepared according to literature methods.$^{1,2}$

tert-Butyl 2-iodobenzoate

To a solution of 2-iodobenzoic acid (4.96 g, 20 mmol) in toluene (100 mL) was added 2 drops of N,N-dimethylformamide and thionyl chloride (1.69 mL, 24 mmol) and the reaction was stirred at 75 ºC overnight. After concentration in vacuo, the 2-iodobenzoyl chloride was added dropwise to a solution of potassium t-butoxide in THF (100 mL) at 0 ºC under nitrogen protection for 0.5 h. Filtration through a Celite pad and concentration in vacuo gave the product as a colorless oil (5.46 g, 90%): $^1$H NMR (400 MHz, CDCl$_3$) δ 1.62 (s, 9H), 7.08-7.13 (m, 1H), 7.35-7.39 (m, 1H), 7.67-7.70 (m, 1H), 7.93-7.95 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 28.1, 82.6, 93.4, 127.8, 130.4, 131.9, 137.4, 140.9, 166.1; FT-IR (neat) ν 2079, 1713, 1296, 1128 cm$^{-1}$; HRMS (ESI$^+$) m/z Calcd for C$_{11}$H$_{14}$IO$_2$ [M+H$^+$] 305.0033 found 305.0035.
(E)-**tert**-Butyl 2-(3-ethoxy-3-oxoprop-1-ethyl)benzoate

\[
\begin{align*}
\text{OEt} & \quad \text{PdCl}_2 (5\%), \text{PPh}_3 (10\%) \quad \text{OEt} \\
\text{Et}_3\text{N}, 110^\circ\text{C} \text{ sealed, overnight} \quad \text{to} \quad \text{OEt}
\end{align*}
\]

To a solution of PdCl\(_2\) (0.159 g, 0.9 mmol) and PPh\(_3\) (0.472 g, 1.8 mmol) in dry Et\(_3\)N (40 mL) under N\(_2\) protection was added *tert*-butyl 2-iodobenzoate (5.46 g, 18 mmol) and ethyl acrylate (2.1 mL, 19.8 mmol). The reaction mixture was stirred at 110\(^\circ\)C in a sealed tube overnight. After cooling and concentrating *in vacuo*, the residue was purified by flash chromatography on silica gel (2.5 cm \(\times\) 20 cm, eluting with ethyl acetate/n-hexane = 1:7, \(R_f\) (EtOAc/hexane (1:5)) = 0.53) to give the corresponding Heck coupling product as a yellow oil (3.78 g, 76%):

\[\text{H NMR (600 MHz, CDCl}_3\text{)} \delta 1.33 (t, J = 7 Hz, 3H), 1.61 (s, 9H), 4.27 (q, J = 7 Hz, 2H), 6.27 (d, J = 16 Hz, 1H), 7.39-7.42 (m, 1H), 7.47-7.50 (m, 1H), 7.54-7.55 (m, 1H), 7.88-7.89 (m, 1H), 8.38 (d, J = 16 Hz, 1H);
\]

\[\text{C NMR (150 MHz, CDCl}_3\text{)} \delta 14.4, 28.3, 60.6, 82.3, 120.5, 127.8, 129.4, 130.7, 131.8, 132.3, 135.8, 144.4, 166.4, 166.7; \text{FT-IR (neat) } \nu 1706, 1636, 1367, 1298, 1268, 1162, 765 \text{ cm}^{-1}; \text{HRMS (ESI}^+\text{) m/z Calcd for C}_{16}H_{20}O_{4}\text{Na [M+Na}^+\text{]} \text{299.1259 found 299.1266.}
\]

(E)-2-(3-Ethoxy-3-oxoprop-1-ethyl)benzoic acid

\[
\begin{align*}
\text{OEt} & \quad \text{CF}_3\text{COOH} \quad \text{OEt} \\
\text{toluene, 50}^\circ\text{C} \text{ 2h, 76%} \quad \text{OEt}
\end{align*}
\]

Trifluoroacetic acid (8 mL) was injected into *tert*-butyl 2-(3-ethoxy-3-oxoprop-1-ethyl)benzoate in toluene (50 mL) and the reaction was stirred at 50\(^\circ\)C for 2 h. After concentration *in vacuo* and purification by flash chromatography on silica gel (2.5 cm \(\times\) 20 cm, eluting with ethyl acetate/n-hexane = 1:3, \(R_f\) (EtOAc/hexane (1:5)) = 0.19), the product was isolated as a colorless oil (3.78 g, 76%): \[\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 1.35 (t, J = 7 Hz, 3H), 4.29 (q, J = 7 Hz, 2H), 6.33 (d, J = 16 Hz, 1H), 7.45-7.49 (m, 1H), 7.56-7.63 (m, 2H), 8.10-8.12 (m, 1H), 8.56 (d, J = 16 Hz, 1H), 10.8 (br.s, 1H); \text{C NMR (150 MHz, CDCl}_3\text{)} \delta 14.4, 60.8, 121.5, 128.3, 128.7, 129.5, 131.8, 133.3, 137.3, 143.9, 166.8, 172.0; \text{FT-IR (neat) } \nu 2982, 2656, 2360, 1706, 1636, 1367, 1298, 1268, 1162, 765 \text{ cm}^{-1}; \text{HRMS (ESI}^+\text{) m/z Calcd for C}_{12}H_{13}O_{4}\text{Na [M+H}^+\text{]} \text{221.0814 found 221.0803.}
\]

(E)-**Methyl** 2-(4-(trifluoromethyl)styryl)benzoate

\[
\begin{align*}
\text{OMe} & \quad \text{PdCl}_2 (5\%), \text{PPh}_3 (10\%) \quad \text{CF}_3 \\
\text{Et}_3\text{N}, 110^\circ\text{C} \text{ sealed, overnight} \quad \text{OMe}
\end{align*}
\]

To a solution of PdCl\(_2\) (0.035 g, 0.2 mmol) and PPh\(_3\) (0.1048 g, 0.4 mmol) in dry
Et$_3$N (4 mL) under N$_2$ protection was added methyl 2-iodobenzoate (0.61 mL, 4 mmol) and 1-((trifluoromethyl)-4- vinyl benzene (0.71 mL, 4.8 mmol). The reaction mixture was stirred at 110 °C in a sealed tube overnight. The reaction was cooled, concentrated in vacuo and the residue purified by flash chromatography on silica gel (2.5 cm × 20 cm, eluting with ethyl acetate/n-hexane = 1:20, Rf (EtOAc/hexane (1:15)) = 0.50) to give the corresponding Heck coupling product as a white solid (1.12 g, 91%): m.p. 73-74 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 3.94 (s, 3H), 7.00 (d, $J = 16$ Hz, 1H), 7.37 (t, $J = 8$ Hz, 1H), 7.53 (d, $J = 8$ Hz, 1H), 7.62 (dd, $J_1 = 4$ Hz, $J_2 = 9$ Hz, 4H), 7.71 (d, $J = 8$ Hz, 1H), 7.98 (d, $J = 8$ Hz, 1H), 8.12 (d, $J = 16$ Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 52.2, 124.4 (q, $J_{CF} = 270$ Hz, CF$_3$), 125.6 (q, $J_{CF} = 4$ Hz, arene C), 127.0, 127.2, 127.8, 128.8, 129.5 (q, $J_{CF} = 32$ Hz, arene C), 129.8, 130.3, 130.9, 132.4, 138.8, 141.0, 167.7; FT-IR (neat) ν 2956, 1713, 1614, 1323, 1105, 951, 821 cm$^{-1}$; HRMS (ESI$^+$) m/z Calcd for C$_{17}$H$_{14}$O$_2$F$_3$ [M+H$^+$] 307.0940 found 307.0941.

(E)-2-(4-(Trifluoromethyl)styryl)benzoic acid

(E)-Methyl 2-(4-(trifluoromethyl)styryl)benzoate (0.98 g, 3.2 mmol) was dissolved in 6 mL of THF:MeOH:H$_2$O (4:1:1, v:v:v) and LiOH (405 mg, 9.6 mmol) was added at room temperature. The reaction mixture was then heated to 50 °C for 2 h. After the reaction mixture was cooled to room temperature, it was acidified to pH 6 using 1M HCl. The product was extracted with ethyl acetate (2 x 20 mL) and then washed with water and brine. The extract was dried over anhydrous MgSO$_4$ and the solvent was evaporated in vacuo to give the stilbene carboxylic acid as a white solid (0.78 g, 83%): m.p. 132-134 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.04 (d, $J = 16$ Hz, 1H), 7.43 (t, $J = 8$ Hz, 1H), 7.60-7.66 (m, 5H), 7.76 (d, $J = 8$ Hz, 1H), 8.14 (d, $J = 8$ Hz, 1H), 8.16 (d, $J = 16$ Hz, 1H), 11.72 (br s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 124.3 (q, $J_{CF} = 270$ Hz, CF$_3$), 125.8 (q, $J_{CF} = 4$ Hz, arene C), 126.7, 127.2, 127.7, 128.0, 129.8 (q, $J_{CF} = 32$ Hz, arene C), 130.3, 130.4, 131.9, 133.5, 139.8, 140.9, 172.2; FT-IR (neat) ν 1682, 1415, 1327, 1108, 1069, 821, 746, 649 cm$^{-1}$; HRMS (ASAP$^+$) m/z Calcd for C$_{16}$H$_{12}$O$_2$F$_3$ [M+H$^+$] 293.0789 found 293.0788.

2.2 General procedure for synthesis of substituted styrene alkynone substrates and product characterisation data

To a solution of substituted 2-vinylbenzoic acid (1 mmol) in dry toluene (10 mL) was added 2 drops of N,N-dimethylformamide and thionyl chloride (0.09 mL, 1.2 mmol)
and the reaction mixture was stirred at 75 °C for 2 h. Evaporation in vacuo gave the acid chloride. To a solution of the acid chloride in THF (10 mL), PdCl$_2$ (17.6 mg, 0.1 mmol), PPh$_3$ (104.8 mg, 0.4 mmol) and CuI (190 mg, 1 mmol) under N$_2$ protection was added stoichiometric amounts of the different alkynes. Finally, Et$_3$N (0.14 mL, 1 mmol) was added dropwise under N$_2$ protection. The reaction was stirred at room temperature for 0.5 h, concentrated in vacuo and the residue was purified by flash chromatography on silica gel to give the corresponding substituted styrene alkyynes.

\[(E)-Ethyl\ 3-(2-hept-2-ynoylphenyl)acrylate\]

![Image](image1.png)

Silica gel purification (2.5 cm × 20 cm, eluted with ethyl acetate/n-hexane = 1:8, R$_f$ (EtOAc/hexane (1:5)) = 0.40) gave a brown yellow oil (45%): $^1$H NMR (600 MHz, CDCl$_3$) δ 0.96 (t, $J = 7$ Hz, 3H), 1.34 (t, $J = 7$ Hz, 3H), 1.47-1.51 (m, 2H), 1.63-1.66 (m, 2H), 2.49 (t, $J = 7$ Hz, 2H), 4.27 (q, $J = 7$ Hz, 2H), 6.29 (d, $J = 16$ Hz, 1H), 7.49-7.51 (m, 1H), 7.55-7.57 (m, 2H), 8.19 (d, $J = 8$ Hz, 1H), 8.41 (d, $J = 16$ Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 13.6, 14.5, 19.1, 22.2, 29.9, 60.7, 81.1, 97.5, 121.6, 128.4, 129.4, 132.6, 133.1, 136.3, 136.4, 143.9, 166.6, 179.2; FT-IR (neat) ν 2203, 1711, 1636, 1242, 1176, 912, 762, 714 cm$^{-1}$; HRMS (ESI$^+$) m/z Calcd for C$_{18}$H$_{21}$O$_3$ [M+H$^+$] 285.1485 found 285.1489.

\[(E,Z)-3-Cyclohexyl-1-(2-(4-methylstyryl)phenyl)prop-2-yn-1-one\]

![Image](image2.png)

Silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:50, R$_f$ (EtOAc/hexane (1:10)) = 0.63) gave a brown oil (21%): $^1$H NMR $^1$H NMR (600 MHz, CDCl$_3$) δ 1.35-1.37 (m, 3H), 1.55-1.62 (m, 3H), 1.72-1.78 (m, 2H), 1.87-1.92 (m, 2H), 2.27 (s, 1H), 2.37 (s, 2H), 2.64-2.69 (m, 1H), 6.63 (d, $J = 12$ Hz, 0.3H), 6.94-6.97 (m, 1H), 6.70-6.73 (m, 1H), 7.17 (d, $J = 8$ Hz, 1H), 7.24 (d, $J = 7$ Hz, 0.3H), 7.32 (dt, $J_1 = 2$ Hz, $J_2 = 7$ Hz, 0.3H), 7.34-7.38 (m, 1H), 7.45-7.46 (m, 1H), 7.52-7.54 (m, 0.7H), 7.72 (d, $J = 8$ Hz, 0.7H), 7.96 (dd, $J = 16$ Hz, 0.7H), 8.15-8.17 (m, 0.7H), 8.21-8.22 (m, 0.3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 21.3, 21.4, 24.9, 24.9, 25.8, 25.8, 29.5, 29.6, 31.8, 31.8, 81.1, 81.6, 99.9, 100.1, 126.6, 127.0, 127.1, 127.2, 128.9, 129.3, 129.5, 129.8, 130.3, 131.5, 131.9, 132.6, 132.6, 132.7, 132.8, 134.0, 134.8, 135.4, 136.0, 136.8, 138.0, 139.3, 139.6, 179.4, 180.3; FT-IR (neat) ν 2924, 2854, 2200, 1630, 1446, 1239, 918, 806 cm$^{-1}$; HRMS (ESI$^+$) m/z Calcd for C$_{24}$H$_{25}$O$_1$ [M+H$^+$] 329.1905 found 329.1900.
(E)-Ethyl 3-(2-(4,4-dimethylpent-2-ynoyl)phenyl)acrylate

Silica gel purification (2.5 cm × 20 cm, eluted with ethyl acetate/n-hexane = 1:5, RF (EtOAc/hexane (1:5)) = 0.50) gave a yellow oil (37%): 1H NMR (700 MHz, CDCl3) δ 1.34 (t, J = 7 Hz, 3H), 1.36 (s, 9H), 4.28 (q, J = 7 Hz, 2H), 6.30 (d, J = 16 Hz, 1H), 7.49-7.51 (m, 1H), 7.55-7.58 (m, 2H), 8.13-8.14 (m, 1H), 8.39 (d, J = 16 Hz, 1H); 13C NMR (176 MHz, CDCl3) δ 14.5, 28.2, 30.2, 60.7, 79.7, 104.6, 121.6, 128.4, 129.4, 132.4, 133.0, 136.2, 136.7, 143.8, 143.8, 166.6, 179.4; FT-IR (neat) ν 2972, 2208, 1713, 1640, 1263, 1176, 759 cm⁻¹; HRMS (ESI⁺) m/z Calcd for C18H21O3 285.1485 [M+H⁺] found 285.1489.

(E)-Ethyl 3-(2-(3-cyclopentylpropioloyl)phenyl)acrylate

Silica gel purification (2.5 cm × 20 cm, eluted with ethyl acetate/n-hexane = 1:5, RF (EtOAc/hexane (1:5)) = 0.38) gave a brown oil (39%): 1H NMR (600 MHz, CDCl3) δ 1.32 (t, J = 7 Hz, 3H), 1.64 (m, 2H), 1.79 (m, 4H), 2.0-2.1 (m, 2H), 2.92 (t, J = 7 Hz, 1H), 4.25 (q, J = 7 Hz, 2H), 6.30 (d, J = 16 Hz, 1H), 7.51-7.53 (m, 1H), 7.57-7.60 (m, 2H), 8.19 (d, J = 8 Hz, 1H), 8.32 (d, J = 16 Hz, 1H); 13C NMR (150 MHz, CDCl3) δ 14.5, 25.6, 30.7, 33.7, 60.9, 80.7, 101.7, 121.6, 128.6, 129.7, 132.9, 133.3, 136.3, 136.8, 144.0, 166.7, 179.5; FT-IR (neat) ν 2956, 2203, 1711, 1635, 1243, 1176, 946, 764 cm⁻¹; HRMS (ESI⁺) m/z Calcd for C19H23O3 297.1491 found 297.1483.

(E)-Ethyl 3-(2-(3-cyclohexylpropioloyl)phenyl)acrylate

Silica gel purification (2.5 cm × 20 cm, eluted with ethyl acetate/n-hexane = 1:5, RF (EtOAc/hexane (1:5)) = 0.50) gave a brown oil (54%): 1H NMR (400 MHz, CDCl3) δ 1.32-1.38 (m, 6H), 1.56-1.65 (m, 3H), 1.74-1.77 (m, 2H), 1.90-1.92 (m, 2H), 2.67-2.71 (m, 1H), 4.27 (q, J = 7 Hz, 2H), 6.29 (d, J = 16 Hz, 1H), 7.48-7.54 (m, 1H), 7.56-7.57 (m, 2H), 8.17-8.19 (m, 1H), 8.40 (d, J = 16 Hz, 1H); 13C NMR (125 MHz,
CDCl$_3$ δ 14.4, 24.8, 25.8, 29.5, 31.7, 60.7, 81.0, 101.0, 121.5, 128.4, 129.4, 132.6, 133.0, 136.2, 143.9, 166.6, 179.3; FT-IR (neat) ν 2930, 2855, 2198, 1710, 1635, 1240, 1175, 915, 763 cm$^{-1}$; HRMS (ESI$^+$) m/z Calcd for C$_{20}$H$_{23}$O$_3$ [M+H$^+$] 311.1647 found 311.1642.

3-Cyclopentyl-1-(2-vinylphenyl)prop-2-yn-1-one

Silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:50, R$_f$ (EtOAc/hexane (1:20) = 0.33) gave a brown oil (41%): $^1$H NMR (400 MHz, CDCl$_3$) δ 1.59-1.67 (m, 2H), 1.75-1.82 (m, 4H), 2.00-2.07 (m, 2H), 2.86-2.93 (m, 1H), 5.37 (dd, $J_1 = 1$ Hz, $J_2 = 11$ Hz, 1H), 5.66 (dd, $J_1 = 1$ Hz, $J_2 = 17$ Hz, 1H), 7.37-7.41 (m, 1H), 7.46-7.53 (m, 2H), 7.56-7.59 (m, 1H), 8.13 (dd, $J_1 = 1$ Hz, $J_2 = 8$ Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 25.4, 30.5, 33.4, 81.0, 100.6, 116.9, 127.5, 127.7, 132.5, 132.9, 135.3, 136.1, 139.5, 180.1; FT-IR (neat) ν 2958, 2869, 2204, 1640, 1242, 768 cm$^{-1}$; HRMS (ESI$^+$) m/z Calcd for C$_{16}$H$_{17}$O$_1$ [M+H$^+$] 225.1274 found 225.1274.

3-Cyclohexyl-1-(2-vinylphenyl)prop-2-yn-1-one

Silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:40, R$_f$ (EtOAc/hexane (1:10) = 0.50) gave a colorless oil (17%) (decomposed partly in CDCl$_3$ overnight): $^1$H NMR (700 MHz, CDCl$_3$) δ 1.34-1.43 (m, 3H), 1.59-1.61 (m, 3H), 1.75-1.78 (m, 2H), 1.91-1.92 (m, 2H), 2.67 (m, 1H), 5.37 (dd, $J_1 = 1$ Hz, $J_2 = 11$ Hz, 1H), 5.67 (dd, $J_1 = 1$ Hz, $J_2 = 17$ Hz, 1H), 7.38-7.40 (m, 1H), 7.49-7.53 (m, 2H), 7.57-7.58 (m, 1H), 8.15 (dd, $J_1 = 1$ Hz, $J_2 = 8$ Hz, 1H); $^{13}$C NMR (176 MHz, CDCl$_3$) δ 24.9, 25.8, 29.6, 31.8, 81.3, 100.0, 116.9, 127.5, 127.7, 132.6, 132.9, 135.3, 136.1, 139.6, 180.1; FT-IR (neat) ν 2926, 2853, 2200, 1640, 1563, 1395, 1801; HRMS (ESI$^+$) m/z Calcd for C$_{17}$H$_{19}$O$_1$ [M+H$^+$] 239.1430 found 239.1431.

(E,Z)-3-Cyclohexyl-1-(2-styrylphenyl)prop-2-yn-1-one

Silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:20, R$_f$ (EtOAc/hexane (1:10) = 0.50) gave a yellow oil (48%): $^1$H NMR (400 MHz, CDCl$_3$) δ 1.24-1.29 (m, 3H), 1.43-1.53 (m, 3H), 1.63-1.69 (m, 2H), 1.77-1.81 (m, 2H), 1.89-1.92 (m, 2H), 1.94-1.96 (m, 2H), 2.00-2.07 (m, 2H), 2.86-2.93 (m, 1H), 5.36 (dd, $J_1 = 1$ Hz, $J_2 = 11$ Hz, 1H), 5.66 (dd, $J_1 = 1$ Hz, $J_2 = 17$ Hz, 1H), 7.37-7.41 (m, 1H), 7.46-7.53 (m, 2H), 7.56-7.59 (m, 1H), 7.68-7.71 (m, 1H), 7.73-7.75 (m, 1H), 8.13 (dd, $J_1 = 1$ Hz, $J_2 = 8$ Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 25.4, 30.5, 33.4, 81.0, 100.6, 116.9, 127.5, 127.7, 132.6, 132.9, 135.3, 136.1, 139.5, 180.1; FT-IR (neat) ν 2958, 2869, 2204, 1640, 1242, 768 cm$^{-1}$; HRMS (ESI$^+$) m/z Calcd for C$_{17}$H$_{19}$O$_1$ [M+H$^+$] 239.1430 found 239.1431.
2.53-2.61 (m, 1H), 6.29 (d, \(J = 12\) Hz, 0.3H), 6.92-7.00 (m, 1.7H), 7.05-7.06 (m, 1H), 7.17-7.23 (m, 1H), 7.28-7.32 (m, 2H), 7.43-7.49 (m, 2H), 7.62-7.64 (m, 1H), 7.92 (d, \(J = 16\) Hz, 1H), 8.07-8.10 (m, 0.7H), 8.13-8.16 (m, 0.3H);

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 24.8, 24.9, 25.8, 25.8, 29.5, 29.6, 31.7, 31.8, 81.5, 84.2, 100.0, 100.2, 127.0, 127.1, 127.2, 127.3, 127.7, 128.0, 128.1, 128.8, 129.4, 130.3, 130.7, 131.5, 131.9, 132.6, 132.7, 132.9, 135.5, 136.0, 136.9, 137.5, 139.1, 139.3, 179.3, 180.2; FT-IR (neat) \(v\) 2928, 2853, 2360, 2200, 1737, 1640, 1447, 1240, 916, 759, 692 cm\(^{-1}\); HRMS (ESI\(^+\)) m/z Calcd for C\(_{23}\)H\(_{23}\)O\(_1\) [M+H\(^+\)] 315.1749 found 315.1739.

3-Cyclohexyl-1-(2-(4-(trifluoromethyl)styryl)phenyl)prop-2-yn-1-one

![Structure 3](image)

After the reaction, the mixture was filtered through a Celite pad which was washed with diethyl ether and concentrated in vacuo to give the crude product as a colorless oil (6%). This material was used in the next step without further purification. \(R_f\) (EtOAc/hexane (1:15)) = 0.50.

4, 4-Dimethyl-1-(2-vinylphenyl)pent-2-yn-1-one

![Structure 4](image)

Silica gel purification (2.5 cm \(\times\) 25 cm, eluted with ethyl acetate/n-hexane = 1:15, \(R_f\) (EtOAc/hexane (1:15)) = 0.41) gave a colorless oil (92%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.36 (s, 9H), 5.37 (d, \(J_1 = 1\) Hz, \(J_2 = 11\) Hz, 1H), 5.66 (dd, \(J_1 = 1\) Hz, \(J_2 = 17\) Hz, 1H), 7.37-7.41 (m, 1H), 7.46-7.53 (m, 2H), 7.56-7.59 (m, 1H), 8.10-8.12 (m, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 28.2, 30.3, 80.0, 103.5, 116.9, 127.5, 127.7, 132.4, 132.8, 135.4, 136.1, 139.5, 180.0; FT-IR (neat) \(v\) 2970, 2853, 2360, 2200, 1737, 1447, 1240, 916, 759, 692 cm\(^{-1}\); HRMS (ESI\(^+\)) m/z Calcd for C\(_{15}\)H\(_{17}\)O\(_1\) [M+H\(^+\)] 213.1274 found 213.1275.

(E)-Ethyl 3-(2-(3-phenylpropioloyl)phenyl)acrylate

![Structure 5](image)

Silica gel (2.5 cm \(\times\) 25 cm, eluted with ethyl acetate/n-hexane = 1:5, \(R_f\) (EtOAc/hexane (1:3)) = 0.54) to give brown oil (15%): \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.32 (t, \(J = 7\) Hz, 3H), 4.26 (q, \(J = 7\) Hz, 2H), 6.34 (d, \(J = 16\) Hz, 1H), 7.41-7.44 (m,
2H), 7.50 (tt, J1 = 2 Hz, J2 = 7 Hz, 1H), 7.54-7.57 (m, 1H), 7.59-7.62 (m, 2H), 7.66-7.68 (m, 2H), 8.30 (d, J = 8 Hz, 1H), 8.47 (d, J = 16 Hz, 1H); 13C NMR (125 MHz, CDCl3) δ 14.4, 60.8, 88.3, 93.7, 120.1, 121.8, 128.6, 128.8, 129.5, 131.1, 132.6, 133.2, 133.4, 136.3, 143.7, 166.6, 178.9; FT-IR (neat) ν 2194, 1710, 1633, 1594, 1267, 1176, 994, 758 cm⁻¹; HRMS (ESI⁺) m/z Calcd for C20H17O3 [M+H⁺] 305.1172 found 305.1175.

(E)-Ethyl 3-(2-(3-cyclohexenylpropioloyl)phenyl)acrylate

Silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:5, RF (EtOAc/hexane (1:5)) = 0.36) gave a yellow oil (39%) (decomposed in CDCl3 overnight); 1H NMR (400 MHz, CDCl3) δ 1.34 (t, J = 7 Hz, 3H), 1.61-1.72 (m, 4H), 2.18-2.22 (m, 2H), 2.22-2.27 (m, 2H), 4.27 (q, J = 7 Hz, 2H), 6.30 (d, J = 16 Hz, 1H), 6.54-6.57 (m, 1H), 7.47-7.51 (m, 1H), 7.54-7.59 (m, 2H), 8.15-8.17 (m, 1H), 8.41 (d, J = 16 Hz, 1H); 13C NMR (125 MHz, CDCl3) δ 14.5, 21.2, 22.1, 26.4, 28.4, 60.7, 86.8, 96.3, 119.2, 121.5, 128.4, 129.4, 132.4, 133.0, 136.2, 136.7, 143.1, 143.9, 166.6, 179.2; HRMS (ESI⁺) m/z Calcd for C20H20O3Na [M+Na⁺] 331.1305 found 331.1307.

(E)-Ethyl 3-(2-(3-cyclopropylpropioloyl)phenyl)acrylate

Silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:5, RF (EtOAc/hexane (1:5)) = 0.25) gave a brown oil (44%); 1H NMR (400 MHz, CDCl3) δ 1.00-1.06 (m, 4H), 1.35 (t, J = 7 Hz, 3H), 1.49-1.56 (m, 1H), 4.28 (q, J = 7 Hz, 2H), 6.29 (d, J = 16 Hz, 1H), 7.47-7.51 (m, 1H), 7.53-7.58 (m, 2H), 8.11-8.14 (m, 1H), 8.39 (d, J = 16 Hz, 1H); 13C NMR (125 MHz, CD2Cl2) δ 10.0, 14.3, 22.9, 31.8, 60.7, 76.9, 101.7, 121.4, 128.4, 129.5, 132.6, 133.1, 136.0, 143.8, 166.6, 178.8; FT-IR (neat): ν 2359, 2206, 1710, 1632, 1566, 1477, 1314, 1251, 1177, 914, 762 cm⁻¹; HRMS (ESI⁺) m/z Calcd for C17H17O3 [M+H⁺] 269.1172 found 269.1174.

2.3 General procedure for substituted styrene alkyne cyclisation and product characterisation data
Procedure A
To AcOH (3 mL) containing Pd(OAc)$_2$ (10 mol \%) and LiCl (4 equiv.), enyne (0.15 mmol) was added. The reaction was heated at 60 °C in air until the substituted styrene alkynone disappeared, as monitored by GC-MS. On cooling, the solvent was removed in vacuo and the residue was purified by flash chromatography to give the product.

Procedure B
To AcOH (3 mL) containing Pd(OAc)$_2$ (10 mol \%) and LiCl (4 equiv.), enyne (0.15 mmol) was added. The reaction was heated at 60 °C under a nitrogen atmosphere. The mixture was stirred until the substituted styrene alkynone disappeared, as monitored by GC-MS. On cooling, the solvent was removed in vacuo and the residue was purified by flash chromatography to give the product.

Procedure C
To CH$_3$CN (3 mL) containing PdCl$_2$ (10 mol \%), substrate (0.15 mmol) was added. The reaction was heated at 80 °C under a nitrogen atmosphere. The mixture was stirred until the substituted styrene alkynone disappeared, as monitored by GC-MS. After cooling, the solvent was removed in vacuo and the residue was purified by flash chromatography to give the product.

1-Butylindeno[2,1-c]pyran-3,9-dione

Procedure A, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:5, $R_f$ (EtOAc/hexane (1:5)) = 0.20) gave a yellow, crystalline product (31\%): m.p. 100-101 ºC; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.96 (t, $J$ = 7 Hz, 3H), 1.41-1.50 (m, 2H), 1.73-1.81 (m, 2H), 3.09 (t, $J$ = 8 Hz, 2H), 6.47 (s, 1H), 7.65 (dt, $J_1$ = 1 Hz, $J_2$ = 8 Hz, 1H), 7.72 (dt, $J_1$ = 1 Hz, $J_2$ = 7 Hz, 1H), 7.82 (dt, $J_1$ = 1 Hz, $J_2$ = 8 Hz, 1H), 7.89 (dt, $J_1$ = 1 Hz, $J_2$ = 8 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 13.8, 22.5, 29.2, 30.4, 102.6, 112.5, 123.5, 124.6, 133.1, 134.9, 139.0, 139.0, 153.5, 161.5, 170.5, 187.7; FT-IR (neat) $\nu$ 2971, 2928, 1732, 1699, 1633, 1578, 1462, 1363, 1140, 906, 874 cm$^{-1}$; HRMS (ESI$^+$) m/z Calcd for C$_{16}$H$_{15}$O$_3$ [M+H$^+$] 255.1021 found 255.1017.

2-(Cyclohexylidenemethyl)-3-(4-methylbenzyl)-1H-inden-1-one

2a

3b
Procedure C, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:80, Rf (EtOAc/hexane (1:10)) = 0.53) gave a brown-red oil (53%): \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta \) 1.56-1.58 (m, 4H), 1.63-1.64 (m, 2H), 2.15 (t, \(J = 5\) Hz, 2H), 2.29 (dt, \(J_1 = 1\) Hz, \(J_2 = 6\) Hz, 2H), 2.31 (s, 3H), 3.85 (s, 2H), 5.74 (s, 1H), 6.84 (d, \(J = 7\) Hz, 1H), 7.09-7.12 (m, 2H), 7.13-7.16 (m, 2H), 7.18-7.20 (m, 1H), 7.20 (dt, \(J_1 = 1\) Hz, \(J_2 = 8\) Hz, 1H), 7.38-7.39 (m, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta \) 21.2, 26.6, 28.0, 28.7, 31.9, 32.9, 37.4, 110.5, 120.4, 122.1, 128.2, 128.6, 129.5, 131.3, 133.4, 133.4, 134.0, 136.4, 145.6, 149.7, 156.0, 197.5; FT-IR (neat) \(\nu \) 2925, 2852, 1709, 1602, 1446, 1161, 810, 744 cm\(^{-1}\); HRMS (ESI\(^+\)) m/z Calcd for C\(_{24}\)H\(_{25}\)O\(_1\) [M+H\(^+\)] 329.1905 found 329.1886.

1-tert-Butylindeno[2,1-c]pyran-3,9-dione

Procedure A, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:10, Rf (EtOAc/hexane (1:5)) = 0.41) gave a white crystalline solid (24 h, 25%, 2 weeks, 67%): m.p. 224-225 °C; \(^1\)H NMR (700 MHz, CDCl\(_3\)) \(\delta \) 1.52 (s, 9H), 6.50 (s, 1H), 7.64 (t, \(J = 8\) Hz, 1H), 7.70 (t, \(J = 7\) Hz, 1H), 7.79 (d, \(J = 8\) Hz, 1H), 7.87 (d, \(J = 8\) Hz, 1H); \(^{13}\)C NMR (176 MHz, CDCl\(_3\)) \(\delta \) 27.3, 38.8, 102.1, 111.9, 122.9, 124.6, 133.0, 134.8, 138.6, 139.0, 155.5, 161.0, 178.4, 186.9; FT-IR (neat) \(\nu \) 2971, 2928, 1732, 1699, 1633, 1578, 1462, 1276, 1254, 1182, 1049, 906, 874 cm\(^{-1}\); HRMS (ESI\(^+\)) m/z Calcd for C\(_{16}\)H\(_{15}\)O\(_3\) [M+H\(^+\)] 255.1021 found 255.1017.

Ethyl 2-(2-(cyclopentylidenemethyl)-1-oxo-1H-inden-3-yl)acetate

Procedure C, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:15, Rf (EtOAc/hexane (1:5) = 0.41) gave a red oil (69%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 1.25 (t, \(J = 7\) Hz, 3H), 1.64-1.71 (m, 4H), 2.30-2.31 (m, 2H), 2.46-2.47 (m, 2H), 3.55 (s, 2H), 4.18 (q, \(J = 7\) Hz, 2H), 5.95 (t, \(J = 2\) Hz, 1H), 7.06 (d, \(J = 7\) Hz, 1H), 7.16-7.20 (m, 1H), 7.31-7.35 (m, 1H), 7.39-7.41 (m, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta \) 14.3, 25.8, 26.9, 32.1, 33.3, 35.0, 61.50, 109.3, 119.7, 122.4, 128.4, 130.7, 133.7, 135.0, 145.5, 148.1, 154.3, 169.3, 196.7; FT-IR (neat) \(\nu \) 2957, 1732, 1710, 1603, 1456, 1162, 1034, 754 cm\(^{-1}\); HRMS (ESI\(^+\)) m/z Calcd for C\(_{19}\)H\(_{21}\)O\(_3\) [M+H\(^+\)] 297.1485 found 297.1487.
1-Cyclopentylindeneno[2,1-c]pyran-3,9-dione

Procedure A, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:5, R_f (EtOAc/hexane (1:5)) = 0.25) gave a white, crystalline solid (34%): m.p. 186-187 °C; ^1H NMR (700 MHz, CDCl_3) δ 1.74-1.75 (m, 2H), 1.88-1.95 (m, 4H), 2.03-2.05 (m, 2H), 4.14-4.19 (m, 1H), 6.44 (s, 1H), 7.64 (dt, J_1 = 1 Hz, J_2 = 7 Hz, 1H), 7.71 (dt, J_1 = 1 Hz, J_2 = 7 Hz, 1H), 7.81 (d, J = 8 Hz, 1H), 7.88 (d, J = 7 Hz, 1H); ^13C NMR (176 MHz, CDCl_3) δ 26.7, 31.4, 39.8, 102.5, 111.8, 123.5, 124.6, 133.1, 134.9, 139.0, 139.2, 153.7, 161.7, 173.5, 188.0; FT-IR (neat) ν 2954, 2866, 1730, 1700, 1650, 1616 cm\(^{-1}\); HRMS (ASAP) m/z Calcd for C_{17}H_{15}O_{3} [M+H]^+ 267.1021 found 267.1011.

Ethyl 2-(2-(cyclohexylidenemethyl)-1-oxo-1H-inden-3-yl)acetate

Procedure C, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:15, R_f (EtOAc/hexane (1:5)) = 0.46) gave a red, crystalline solid (76%): m.p. 82-84 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.25 (t, J = 7 Hz, 3H), 1.54-1.56 (m, 4H), 1.60-1.64 (m, 2H), 2.08-2.11 (m, 2H), 2.27-2.30 (m, 2H), 3.53 (s, 2H), 4.19 (q, J = 7 Hz, 2H), 5.67 (s, 1H), 7.05-7.07 (m, 1H), 7.17-7.20 (m, 1H), 7.32-7.36 (m, 1H), 7.40-7.42 (m, 1H); ^13C NMR (101 MHz, CDCl_3) δ 14.3, 26.5, 28.0, 28.6, 31.6, 33.4, 37.4, 61.5, 110.2, 119.8, 122.4, 128.5, 130.7, 133.7, 134.6, 145.4, 149.1, 150.3, 169.3, 197.2; FT-IR (neat): ν 2931, 2852, 1723, 1705, 1605, 1458, 1249, 1026, 774, 736 cm\(^{-1}\); HRMS (ASAP) m/z Calcd for C_{20}H_{22}O_{3} [M] 310.1569 found 310.1546.

2-(Cyclopentylidenemethyl)-3-methyl-1H-inden-1-one

Procedure C, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:15, R_f (EtOAc/hexane (1:20)) = 0.34) gave a red oil (94%): ^1H NMR (500 MHz, CDCl_3) δ 1.68-1.71 (m, 4H), 2.10 (s, 3H), 2.27-2.28 (m, 2H), 2.48-2.49 (m, 2H), 5.96 (s, 1H), 7.04 (d, J = 7 Hz, 1H), 7.17 (t, J = 7 Hz, 1H), 7.33 (dt, J_1 = 1 Hz, J_2 = 8 Hz, 1H), 7.37 (d, J = 7 Hz, 1H); ^13C NMR (125 MHz, CDCl_3) δ 13.0,
25.9, 26.9, 32.3, 34.8, 109.9, 118.9, 121.8, 128.4, 131.0, 133.1, 133.5, 146.7, 152.4, 153.1, 197.4; FT-IR (neat) ν 2924, 1706, 1456, 1383, 962, 754 cm⁻¹; HRMS (ESI⁺) m/z Calcd for C₁₄H₁₇O₁ [M+H⁺] 225.1274 found 225.1274.

2-(Cyclohexylidenemethyl)-3-methyl-1H-inden-1-one

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3g
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Procedure C, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:20, Rf (EtOAc/hexane (1:15)) = 0.53) gave a red oil (88%): ¹H NMR (400 MHz, CDCl₃) δ 1.56-1.64 (m, 6H), 2.09-2.10 (m, 5H), 2.29 (t, J = 6 Hz, 2H), 5.70 (s, 1H), 7.05 (d, J = 7 Hz, 1H), 7.18 (t, J = 8 Hz, 1H), 7.34 (dt, J₁ = 1 Hz, J₂ = 7 Hz, 1H), 7.39 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 13.0, 26.6, 27.8, 28.6, 31.7, 37.4, 110.9, 119.0, 121.9, 128.4, 131.0, 132.6, 133.5, 146.6, 148.6, 154.0, 197.8; FT-IR (neat) ν 2926, 2852, 1706, 1610, 1456, 1382, 1082, 754 cm⁻¹; HRMS (ESI⁺) m/z Calcd for C₁₆H₁₇O₁ [M+H⁺] 239.1430 found 239.1431.

3-Benzyl-2-(cyclohexylidenemethyl)-1H-inden-1-one

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3h
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Procedure C, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:80, Rf (EtOAc/hexane (1:10)) = 0.57) gave a red oil (78%): ¹H NMR (400 MHz, CDCl₃) δ 1.55-1.56 (m, 3H), 1.60-1.63 (m, 3H), 2.14 (t, J = 6 Hz, 2H), 2.28 (t, J = 6 Hz, 2H), 3.89 (s, 2H), 5.74 (s, 1H), 6.82 (d, J = 7 Hz, 1H), 7.12 (dt, J₁ = 1 Hz, J₂ = 8 Hz, 1H), 7.17-7.30 (m, 6H), 7.38-7.40 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 26.5, 28.0, 28.7, 31.9, 33.3, 37.4, 110.4, 120.4, 122.2, 126.8, 128.2, 128.7, 128.9, 131.3, 133.4, 133.5, 137.2, 145.5, 149.8, 155.7, 197.5; FT-IR (neat) ν 2927, 2852, 1719, 1602, 1453, 760, 724, 697 cm⁻¹; HRMS (ESI⁺) m/z Calcd for C₂₃H₂₃O₁ [M+H⁺] 315.1749 found 315.1724.

2-(Cyclohexylidenemethyl)-3-(4-(trifluoromethyl)benzyl)-1H-inden-1-one

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3i
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Electronic Supplementary Material (ESI) for Chemical Communications
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Procedure C, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:30, Rf (EtOAc/hexane (1:15)) = 0.47) gave a red solid (98%): m.p. 123-125 °C; 1H NMR (400 MHz, CDCl3) δ 1.53-1.57 (m, 4H), 1.60-1.64 (m, 2H), 2.13 (t, J = 6 Hz, 2H), 2.28 (t, J = 6 Hz, 2H), 3.9 (s, 2H), 5.7 (s, 1H), 6.79 (d, J = 7 Hz, 1H), 7.15 (dt, J1 = 1 Hz, J2 = 8 Hz, 1H), 7.21-7.25 (m, 1H), 7.38 (d, J = 8 Hz, 2H), 7.41-7.43 (m, 1H), 7.55 (d, J = 8 Hz, 2H); 13C NMR (150 MHz, CDCl3) δ 26.5, 28.0, 28.7, 32.0, 33.0, 37.4, 110.2, 120.1, 122.5, 124.3 (q, JCF = 270 Hz, CF3), 125.8 (q, JCF = 32 Hz, arene C), 128.5, 129.0, 129.3 (q, JCF = 32 Hz, arene C), 131.1, 133.6, 134.1, 141.4, 145.1, 150.4, 154.3, 197.1; FT-IR (neat) ν 2926, 2854, 1709, 1602, 1448, 1323, 1124, 1067, 1020, 848, 752 cm⁻¹; HRMS (ESI⁺) m/z Calcd for C34H32O3P3 [M+H⁺] 383.1617 found 383.1617.

3-Methyl-2-(3-methylbut-2-en-2-yl)-1H-inden-1-one

Procedure C, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:20, Rf (EtOAc/hexane (1:10)) = 0.50) gave a brown oil (98%): 1H NMR (400 MHz, CDCl3) δ 1.58 (s, 3H), 1.82 (s, 6H), 2.03 (s, 3H), 7.06 (d, J = 7 Hz, 1H), 7.19 (t, J = 7 Hz, 1H), 7.35 (t, J = 8 Hz, 1H), 7.39 (d, J = 7 Hz, 1H); 13C NMR (101 MHz, CDCl3): δ 12.5, 18.6, 20.3, 22.6, 119.0, 120.1, 121.8, 128.4, 131.0, 132.3, 133.4, 138.3, 146.2, 154.1, 197.7; FT-IR (neat) ν 2914, 1702, 1608, 1455, 1380, 1324, 1081, 755, 719 cm⁻¹; HRMS (ESI⁺) m/z Calcd for C13H11O1 [M+H⁺] 213.1279 found 213.1262.

2.4 Procedure for Luche reduction of cyclisation product and characterisation data

3-Methyl-2-(3-methylbut-2-en-2-yl)-1H-inden-1-ol

To MeOH (10 mL) containing cerium(III) chloride heptahydrate (1.1 equiv.) and substrate (0.45 mmol) was added sodium borohydride (1.1 equiv.) at 0 °C. The reaction was stirred at room temperature under an N₂ atmosphere for 0.5 h. Then, the solvent was removed in vacuo. The residue was purified by flash chromatography (2.5 cm × 8 cm, eluted with ethyl acetate/n-hexane = 1:5, Rf (EtOAc/hexane (1:2)) = 0.62) to give a brown oil (90%): 1H NMR (400 MHz, CDCl3) δ 1.65 (d, J = 1 Hz, 3H), 1.86 (s, 3H), 1.89 (s, 3H), 1.89 (s, 3H), 5.21 (s, 1H), 7.17-7.22 (m, 2H), 7.32 (dt, J1 = 1 Hz, J2 = 7 Hz, 1H), 7.50 (d, J = 8 Hz, 1H); 13C NMR (151 MHz, CDCl3) δ 11.5, 18.8, 20.5, 22.4, 77.2, 118.9, 123.1, 123.2, 125.6, 128.5, 131.1, 133.9, 144.7, 144.7, 147.5; FT-IR (neat) ν 1725, 1606, 1436, 1372, 1177, 1088, 1005, 752, 731, 688, 630 cm⁻¹.
2.5 References

3. $^1$H and $^{13}$C-NMR spectra for new compounds
$^1$H COSY (600 MHz)

$^{13}$C DEPT 135 (101 Mhz)
$^{1}H-^{13}C$ HSQC (600 MHz)

$^{1}H-^{13}C$ HMBC (600 MHz)
$^1$H COSY (400 MHz)

$^1$H-$^{13}$C HSQC (600 MHz)
$^1$H-$^{13}$C HMBC (600 MHz)
$^1$H COSY (700 MHz)

$^1$H-$^{13}$C HSQC (700 MHz)
$^1$H-$^{13}$C HMBC (700 MHz)
$^1$H COSY (700 MHz)

$^1$H-$^{13}$C HSQC (700 MHz)
$^1$H-$^{13}$C HMBC (700 MHz)
$^1$H COSY (400 MHz)

$^1$H NOESY (500 MHz)
$^1$H-$^{13}$C HSQC (600 MHz)

$^1$H-$^{13}$C HMBC (600 MHz)
$^{19}\text{FNMR} (376\text{ MHz})$
$^1$H COSY (400 MHz)

$^1$H-$^{13}$C HSQC (600 MHz)
$^1$H-$^{13}$C HMBC (600 MHz)
\(^1\)H COSY (600 MHz)

\(^1\)H NOESY (600 MHz)
$^{1}$H-$^{13}$C HSQC (600 MHz)

$^{1}$H-$^{13}$C HMBC (600 MHz)
4. X-ray molecular structures

Figure S1 Molecular structure of 1-butylindeno[2,1-c]pyran-3,9-dione (2a) CCDC-852796

Figure S2 Molecular structure of 1-tert-butylindeno[2,1-c]pyran-3,9-dione (2c) CCDC-857641
Figure S3 Molecular structure of 1-cyclopentylindeno[2,1-c]pyran-3,9-dione (2d)
CCDC-857642

Figure S4 Molecular structure of 1-phenylindeno[2,1-c]pyran-3,9-dione (2k)
CCDC-895772
Figure S5  Molecular structure of ethyl 2-(2-(cyclohexylidemethyl)-1-oxo-1H-inden-3-yl)acetate (3e)
CCDC-852797